

# Microwave-Assisted Shape-Controlled Bulk Synthesis of Noble Nanocrystals and Their Catalytic Properties

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**ABSTRACT:** Bulk and shape-controlled synthesis of gold (Au) nanostructures with various shapes such as prisms, cubes, and hexagons is described that occurs via microwave-assisted spontaneous reduction of noble metal salts using an aqueous solution of  $\alpha$ -D-glucose, sucrose, and maltose. The expeditious reaction is completed under microwave irradiation in 30–60 s and can be applied to the generation of nanospheres of silver (Ag), palladium (Pd), and platinum (Pt). The noble nanocrystals undergo catalytic oxidation with monomers such as pyrrole to generate noble nanocomposites, which have potential functions in catalysis, biosensors, energy storage systems, nanodevices, and other ever-expanding technological applications.

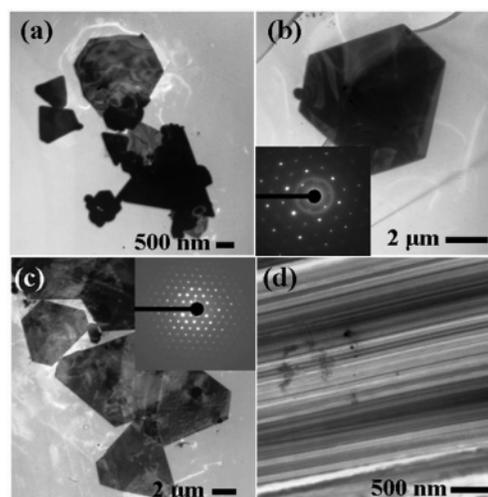
## Introduction

The metal nanostructures have been the focus of intensive research in the past several decades due to their potential applications in fabricating electronic, optical, optoelectronic, and catalytic properties tailored by controlling their size, shape, composition, and crystallinity.<sup>1–7</sup> Among these parameters, shape control has proven to be as effective as size control in fine-tuning the properties and functions of metal nanostructures.<sup>8–19</sup> Although several wet chemical approaches have particle size control for various metallic systems in place, there has been limited success in gaining bulk control over the shape of nanocrystals.<sup>20–23</sup> Herein, we describe a simple and straightforward method for bulk and shape-controlled synthesis of prisms, cubes, hexagons, and spherical nanostructures of noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) by microwave (MW)-assisted spontaneous reduction of noble metal salts using  $\alpha$ -D-glucose, sucrose, and maltose in aqueous solution. Currently, there is a growing need to develop such ecofriendly processes<sup>24–28</sup> that avoid the use of toxic chemicals in the preparative protocol with increased emphasis on the synthesis of nanoparticles using greener methods.<sup>28</sup> Recently, we accomplished a shape-selective synthesis of noble nanoparticles and nanowires using vitamin B<sub>2</sub> without using any harmful reducing agents, such as sodium borohydride (NaBH<sub>4</sub>) or hydroxylamine hydrochloride, and or surfactants.<sup>25</sup> Vitamin B<sub>2</sub> was used as reducing agent as well as capping agent due to its high water solubility, biodegradability, and low toxicity compared with other reducing agents. In continuation of our efforts to develop novel greener methods to synthesize noble nanostructures, herein we report an environmentally benign approach that provides facile entry to production of multiple shaped noble nanostructures, which may find widespread technological and medicinal applications.

## Experimental Procedures

HAuCl<sub>4</sub>·4H<sub>2</sub>O and  $\alpha$ -D-glucose were obtained from Aldrich Chemical Co. and used as received in deionized water. In a typical experiment, an aqueous solution of HAuCl<sub>4</sub> (5 mL, 0.01 N) was placed in a 20 mL glass vessel and then mixed with 300 mg of  $\alpha$ -D-glucose. The reaction mixture was exposed to high-intensity microwave irradiation (1000 W, Panasonic MW oven equipped with inverter technology) for 30–45 s.

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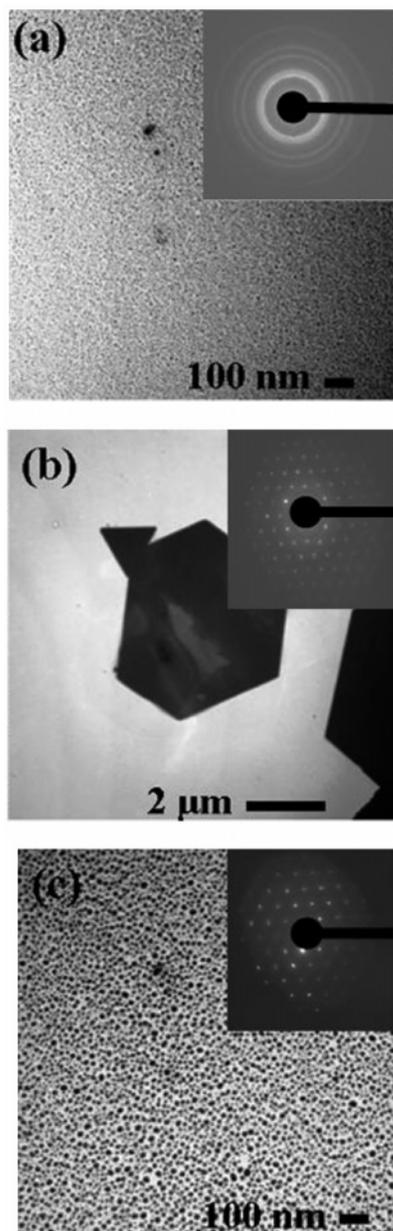


**Figure 1.** TEM images of Au nanostructures synthesized (low concentration of sugar) using microwave irradiation with (a) sucrose, (b)  $\alpha$ -D-glucose, or (c, d) maltose. The insets show corresponding electron diffraction patterns.

Similarly, experiments (see Supporting Information, section S1) were conducted using 0.01 N PtCl<sub>4</sub>, 0.01 N PdCl<sub>2</sub> and 0.1 N AgNO<sub>3</sub>. In the cases of PdCl<sub>2</sub> and AgNO<sub>3</sub>, 300 mg of poly(vinyl pyrrolidone) (PVP) was added to prevent aggregation and the formation of silver mirror (Tollen's process) on the surface of the glass walls.

## Results and Discussion

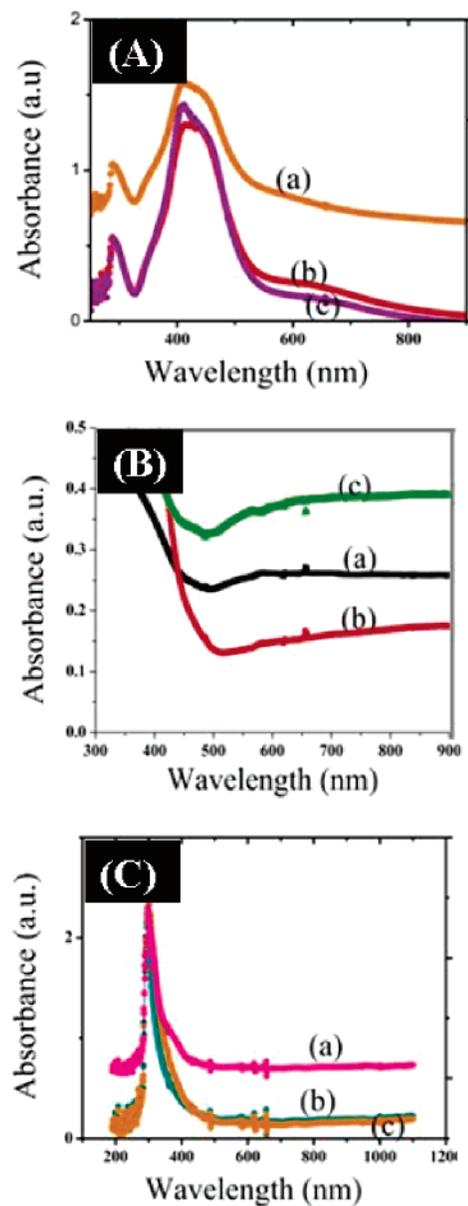
Microwave irradiation provides rapid and uniform heating of reagents, solvents, and intermediates.<sup>26–28</sup> This rapid MW heating also provides uniform nucleation and growth conditions, leading to homogeneous nanomaterials with smaller sizes. Power dissipation is fairly uniform throughout with “deep” inside-out heating of the polar solvents, which leads to a better crystallinity. Different techniques have been developed to generate metal nanoparticles. There are two general strategies to obtain materials on the nanoscale: a bottom up method where the atoms (produced from reduction of ions) are assembled to generate nanostructures or a top down method where material is removed from the bulk material, leaving only the desired nanostructures. Top down techniques suffer from the need to remove large amounts of material, while bottom up techniques suffer from poor monodispersity due to the need to arrest growth



**Figure 2.** TEM images of Au nanostructures synthesized using a high concentration of sugar: (a)  $\alpha$ -D-glucose; (b) maltose; (c) sucrose. The insets show corresponding electron diffractions.

at the same point for all the nanoparticles. Bottom up synthesis techniques usually employ an agent to stop growth of the particle at the nanoscale along with reducing agent.<sup>29</sup> Capping materials, such as a surfactant or polymer are used in this technique to prevent aggregation and precipitation of the metal nanoparticles out of solution. Choice of the reduction technique, time, and capping material determines the size and shape of the nanoparticles generated.<sup>29</sup> However, in the present study sugars serve a multifunctional role, that is, reducing agent as well as capping agent, which precludes the need for separate capping or the use of surfactants to prevent aggregation.

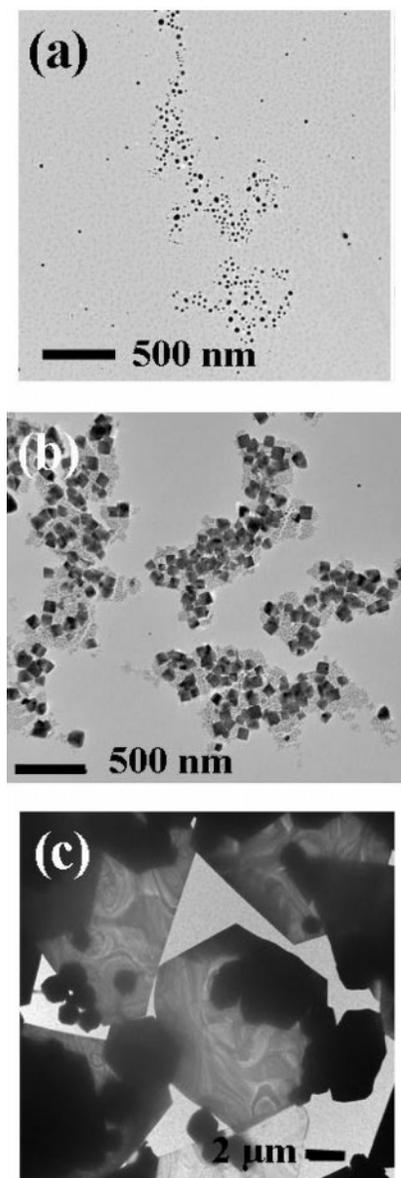
Formation of prisms, cubes, and hexagons occurred (see Figure 1) when the sugar solution was used at a lower concentration. The inset in Figure 1b shows the electron diffraction pattern for the individual nanoprism by directing the electron beam perpendicular to one of its hexagonal faces, indicating that each nanoplate was a single crystal. Three sets of spots could be identified based on their  $d$ -spacing: The



**Figure 3.** UV spectra of (A) Ag with (a) sucrose, (b)  $\alpha$ -D-glucose, or (c) maltose; (B) Au with (a) sucrose, (b)  $\alpha$ -D-glucose, or (c) maltose; and (C) Pt with (a) maltose, (b)  $\alpha$ -D-glucose, or (c) sucrose.

strongest spots could be indexed to the  $\{220\}$  reflection of face-centered cubic (fcc) gold. The outer set corresponded to the  $\{422\}$  Bragg reflections. These two sets of reflections were both allowed by a fcc lattice. The third set with very weak spots could be indexed to  $(1/3)\{422\}$  reflection, which is normally forbidden by a fcc lattice. The surface morphology of these Au nanostructures obtained using maltose appeared as several nanowires aligned together to form a sheet (see Figure 1d).

At higher sugar concentrations, however, the formation of spherical particles was accomplished with  $\alpha$ -D-glucose and sucrose in aqueous media within 30–45 s of MW irradiation. In contrast, Au nanostructures with different morphologies such as prism, cube, and hexagon nanostructures were obtained using maltose (see Figure 2 and Supporting Information, Figure S2, for SEM images and Figure 3 for UV spectra). Electron diffraction patterns for Au nanostructures suggested that they had crystallized in the fcc structure. The as-synthesized Ag nanoparticles exhibited an extinction spectrum displayed as a broad curve at 415 nm (see Figure 3a). Au (Figure 3b) displayed

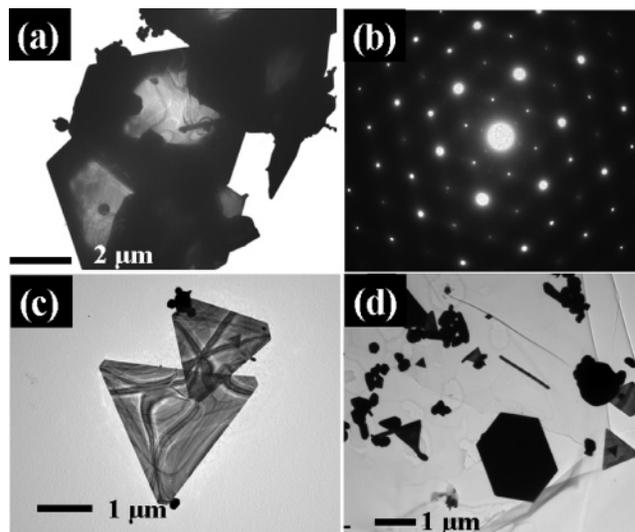


**Figure 4.** TEM images of Au nanostructures synthesized using an oil bath at a temperature of 78 °C with (a)  $\alpha$ -D-glucose, (b) sucrose, or (c) maltose.

a broad absorption from 550 to 900 nm, whereas Pt (Figure 3c) and Pd (not shown) absorbed continuously in the UV region.

The control experiments were conducted in an oil bath at 78 and 100 °C, the temperature range reached in MW experiments, to see the effect of heat source and time taken for completion of the reaction (see Figures 4 and 5). It was found that the time required for completion of the reaction was comparatively much longer at the same temperature as that reached in microwave-assisted procedures; the measured temperature inside the reaction mixture after MW irradiation for 30–40 s was 78–80 °C.

In oil bath at 78 °C, the reaction was completed after 2 h, and an increase in temperature up to 100 °C reduced the reaction time by half an hour. There was a significant difference in particle morphology at least in one case of sugar as shown in Figure 4; sucrose yielded uniform cubes of sizes ranging from 40 to 60 nm. However, no discernible difference was observed for  $\alpha$ -D-glucose and maltose except for the reaction time and growth in particle size. Increase in temperature to 100 °C yielded various shapes such as prisms, cubes, and hexagons irrespective of sugar concentrations (see Figure 5).



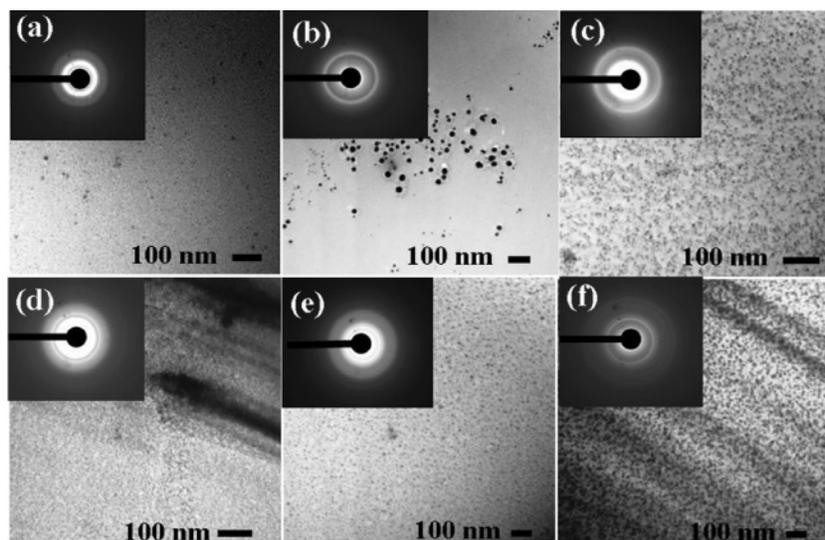
**Figure 5.** TEM images of Au nanostructures synthesized using an oil bath at a temperature of 100 °C with (a)  $\alpha$ -D-glucose with (b) selected area electron diffraction (SAED) of the sample in panel a and nanostructures synthesized with (c) sucrose and (d) maltose.

This method is general and can be extended to other noble metals such as Ag, Pd, and Pt. However, addition of poly(vinyl pyrrolidone) (PVP) is required for Ag and Pd in order to overcome the aggregation observed in these cases. Platinum formed nanospheres ranging from 5 to 10 nm depending upon the sugar solution used (see Supporting Information, Figure S3). Using high concentrations of sugar and PVP as capping agent, it was possible to control the particle size of Ag and Pd from as low as 2 nm up to 15 nm depending upon the sugar solution used (see Figure 6 for TEM images). Ag formed average particle sizes of 3.43, 5.03, and 15.2 nm for  $\alpha$ -D-glucose, maltose, and sucrose, respectively, and Pd formed average particle sizes of 9.13, 7.39, and 9.10 nm for  $\alpha$ -D-glucose, maltose, and sucrose, respectively. Ag and Pd nanoparticles crystallized in fcc symmetry as shown in the insets of Figure 6. In the cases of Au and Pt, addition of PVP capping agent was not necessary to prevent aggregation since the surface passivation of Au and Pt is low when compared with Ag and Pd and the presence of sugar was enough for reduction and capping of nanostructures.

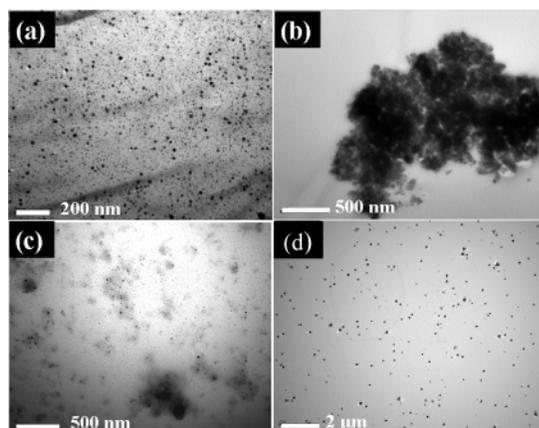
These noble metals (synthesized in presence of PVP) underwent catalytic reaction with pyrrole at room temperature to generate polypyrrole nanocomposites (see Figures 7 and 8), which have potential functions in catalysis, biosensors, energy storage systems, nanodevices, and other ever-expanding technological applications.

## Conclusions

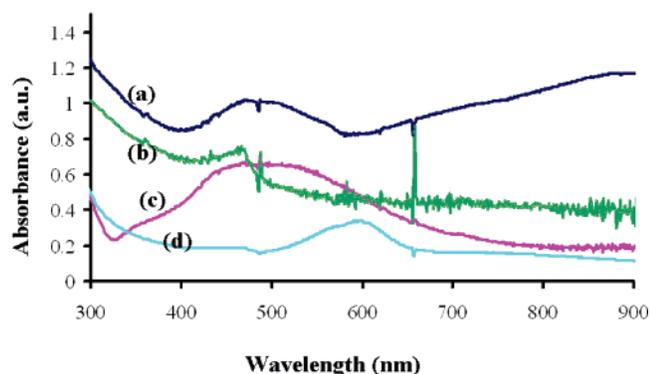
In summary, we have shown that nanostructures of noble metals with varying shapes and sizes can be generated from aqueous sugar solutions using MW irradiation. Specifically, (i) bulk and shape-controlled synthesis of nanostructures of noble metals such as Ag, Pd, and Pt with particle sizes from 2 to 15 nm was achieved depending upon the sugar solution; (ii) at higher concentration, prisms, cubes, and hexagons of Au were obtained using maltose and spherical nanostructures were obtained using  $\alpha$ -D-glucose and sucrose; (iii) by decreasing the sugar concentration, it was possible to synthesize prisms, cubes, and hexagons of Au nanostructures in bulk quantity irrespective of the sugar used for the preparation; and (iv) this method is general, ecofriendly, and completed in a few seconds to afford



**Figure 6.** TEM images of Ag and Pd nanostructures synthesized using MW irradiation in presence of poly(vinyl pyrrolidone) as capping agent: (a) Ag with  $\alpha$ -D-glucose; (b) Ag with sucrose; (c) Ag with maltose; (d) Pd with  $\alpha$ -D-glucose; (e) Pd with maltose; (f) Pd with sucrose. The insets show corresponding electron diffraction patterns.



**Figure 7.** Polypyrrole nanocomposites derived from (a) Pd, (b) Pt, (c) Au, and (d) Ag noble nanostructures synthesized using MW irradiation in presence of  $\alpha$ -D-glucose and poly(vinyl pyrrolidone) (PVP).



**Figure 8.** UV spectra of polypyrrole nanocomposites with (a) Pd, (b) Pt, (c) Ag, and (d) Au.

nanostructures of different shapes and sizes that may find useful roles in catalysis, biosensors, energy storage systems, nanodevices, and other ever-expanding technological applications.

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**Supporting Information Available:** Synthetic procedures and SEM and TEM figures of generated products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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